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(54) **PREPARATION DE COPOLYMERES A BASE DE**

(METH)ACRYLATE SOLUBLES DANS LES ALCALIS

(54) **PREPARATION OF ALKALI-SOLUBLE (METH)ACRYLATE-
BASED COPOLYMERS**

(57) Méthode pour préparer des copolymères à base de (méth)acrylate solubles dans les alcalis, par polymérisation en émulsion de radicaux libres à un pH < 4, avec ajustement, après la polymérisation, du pH de la dispersion entre 4 et 7, par addition d'une base.

(57) A process for preparing alkali-soluble (meth)acrylate-based copolymers by free-radical emulsion polymerization at a pH <4, which involves adjusting the pH of the dispersion after polymerization to a level within the range from 4 to 7 by adding a base.

PREPARATION OF ALKALI-SOLUBLE (METH)ACRYLATE-BASED COPOLYMERS

Abstract

A process for preparing alkali-soluble (meth)acrylate-based copolymers by free-radical emulsion polymerization at a pH <4, which involves adjusting the pH of the dispersion after polymerization to a level within the range from 4 to 7 by adding a base.

PREPARATION OF ALKALI-SOLUBLE (METH)ACRYLATE-BASED COPOLYMERS

- 5 The present invention relates to a process for preparing (meth)acrylate-based copolymers which are soluble in the alkaline range by free-radical emulsion polymerization at a pH <4 and to the copolymers obtainable by this process, and their use.
- 10 (Meth)acrylate-based copolymers which are soluble in water in the alkaline range are frequently employed in the field of cosmetology as hairsetting agents. For example, EP-A-379 082 describes hairsetting compositions which as film former comprise copolymers having a K value of from 10 to 50 which are composed
- 15 of from 75 to 99 % by weight of t-butyl acrylate and/or t-butyl methacrylate, from 1 to 25 % by weight of acrylic acid and/or methacrylic acid, and from 0 to 10 % by weight of a further free-radically copolymerizable monomer. For use in cosmetology, all or some of the copolymer carboxyls are neutralized by means
- 20 of amines.

DE-A-43 14 305 describes hairsetting compositions whose film former comprises copolymers of the type specified in EP-A-379 082 composed of from 30 to 72 % by weight of t-butyl acrylate and/or

25 t-butyl methacrylate, from 10 to 28 % by weight of acrylic acid and/or methacrylic acid, and from 0 to 60 % by weight of a free-radically copolymerizable monomer or of a free-radically copolymerizable monomeric mixture, at least one of these monomers producing a homopolymer having a glass transition temperature

30 <30°C.

EP-A-646 606 describes alkali-soluble copolymers of low molecular weight which are composed of from 25 to 75 % by weight of a water-insoluble monoethylenically unsaturated aromatic monomer

35 and from 25 to 75 % by weight of (meth)acrylic acid. Copolymers of this type are used in printing pastes, surface treatment compositions, coating compositions, adhesive compositions and paper-coating compositions. These copolymers are prepared by emulsion polymerization at a pH ≤ 4.5 using a molecular weight

40 regulator.

If the abovementioned copolymers are to be employed as hairsetting agents, they must wash off readily from the hair.

45 This is generally achieved by making the copolymers soluble in water through neutralization of some or all of the carboxyls, generally using an alkali metal hydroxide or, preferably, an organic amine. The pH of a solution of a partially or completely

neutralized copolymer is, in general, in the range from 8.0 to 9.5.

5 The copolymers can be prepared by solution, suspension or emulsion polymerization, the latter having the advantage that the resulting dispersion can be freed from residual monomers and odorous substances by means of physical deodorization, for example by passing steam into the dispersion.

10 However, the dispersions obtained by emulsion polymerization have the following two disadvantages:

- 15 a) Their shear stability is inadequate. In the industrial apparatus commonly used for physical deodorization, the dispersion is subject to strong shear. In insufficiently shear-stable dispersions this has the consequence of partial or complete coagulation and/or sedimentation and/or of deposits in the apparatus.
- 20 b) The dispersions obtained by polymerization are acidic, owing to the presence of the carboxyls, and in the course of 6-month storage tests show a reduction in pH by about 0.3 units. In practice this is undesirable and unacceptable.

25 It is an object of the present invention to provide a process for preparing alkali-soluble (meth)acrylate-based copolymers by free-radical emulsion polymerization which provides a copolymer dispersion of sufficient stability. In particular, it is intended that the copolymer dispersion will have better shear stability and storage stability than the prior art dispersions.

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We have found that this object is achieved, surprisingly, if the pH of the dispersion obtained on polymerization is adjusted to a level within the range from 4 to 7.

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The present invention accordingly provides a process for preparing alkali-soluble (meth)acrylate-based copolymers by free-radical emulsion polymerization at a pH <4, which comprises adjusting the pH of the dispersion after polymerization to a
40 level within the range from 4 to 7 by adding a base.

Polymerization starts from a monomer mixture containing at least one acrylate and/or methacrylate or a mixture thereof and at least one monomer which is copolymerizable therewith and includes
45 at least one carboxyl.

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Suitable acrylates and methacrylates are those which lend themselves to emulsion polymerization, especially esters of acrylic or methacrylic acid with C₁-C₆ alcohols such as methanol, ethanol, isopropanol, n-propanol, n-butanol, sec-butanol, 5 iso-butanol, tert-butanol and the like. Preference is given to t-butyl acrylate or t-butyl methacrylate.

The carboxyl-containing monomers are preferably acrylic, methacrylic, maleic, itaconic or crotonic acid.
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Particular preference is given to acrylic acid, methacrylic acid or a mixture thereof.

15 To modify the properties of the copolymer it is also possible, if desired, to copolymerize at least one further monomer. This monomer, or at least one of these monomers, should produce a homopolymer having a glass transition temperature ≤ 30 °C. Preferred such monomers are C₁-C₁₈-alkyl acrylates or C₁-C₁₈-alkyl (meth)acrylates or N-C₁-C₁₈-alkylacrylamides or N-C₁-C₁₈-alkyl 20 (meth)acrylamides, especially N-C₁-C₄-alkylacrylamides or -methacrylamides or mixtures of two or more of these monomers. C₁-C₄-alkyl in the abovementioned (meth)acrylates and (meth)acrylamides is suitably methyl, ethyl, n-propyl, isopropyl, 25 n-butyl, isobutyl, sec-butyl or t-butyl. Particularly preferred monomers are ethyl acrylate or a mixture thereof with N-t-butylacrylamide.

In a particularly preferred embodiment, the copolymers are
30 obtained by free-radical polymerization of

- a) from 30 to 72 % by weight of t-butyl acrylate or t-butyl methacrylate or a mixture thereof,
- b) from 10 to 28 % by weight of acrylic acid or methacrylic acid 35 or a mixture thereof, and
- c) from 0 to 60 % by weight of a free-radically copolymerizable monomer or mixture of monomers, at least one of these monomers producing a homopolymer with a glass transition temperature ≤ 30 °C.

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It is preferred to use from 50 to 72 % by weight and, in particular, from 60 to 70 % by weight of the monomer a),

45 from 10 to 25 % by weight and, in particular, from 15 to 23 % by weight of the monomer b), and

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from 3 to 38 % by weight and, in particular, from 7 to 25 % by weight of the monomer c).

5 The particularly preferred copolymers are described in DE-A-43 14 305, the entire content of which is incorporated herein by reference.

10 The K values of the novel polymers are generally in the range from 10 to 90, preferably from 10 to 60 and, in particular, from 15 to 50. The desired K value can be established conventionally by choosing the polymerization conditions, for example the temperature of polymerization and the concentration of initiator. The K value can also be reduced by using regulators, such as
15 aldehydes, halogen or sulfur compounds, examples being formaldehyde, acetaldehyde, bromotrichloromethane, mercaptoethanol, 2-ethylhexyl thioglycolate, thioglycolic acid or dodecyl mercaptan. The amounts of regulators, based on the monomers to be polymerized, are generally up to 10 % by weight,
20 preferably from 0.1 to 5 % by weight.

The K values are measured by the method of Fikentscher, Cellulosechemie, Volume 13 (1932) 58-64 at 25°C in 1 % strength by weight solution in ethanol and are a measure of the molecular
25 weight.

The glass transition temperature of the novel copolymers is usually in the range from 50 to 130°C, in particular from 60 to 100°C.

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Copolymers are prepared conventionally using initiators such as peroxo or azo compounds, examples being dibenzoyl peroxide, t-butyl perpivalate, t-butyl per-2-ethylhexanoate, di-t-butyl peroxide, t-butyl hydroperoxide,
35 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, alkali metal or ammonium persulfates, azobisisobutyronitrile, 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobis(2,4-dimethylvaleronitrile), 1,1'-azobis(1-cyclohexanecarbonitrile),
40 2,2'-azobis(2-amidinopropane) salts, 4,4'-azobis(4-cyanovaleric acid) or 2-(carbamoylazo)isobutyronitrile, etc., hydrogen peroxide or redox initiators. These initiators are usually employed in amounts of up to 10 % by weight, preferably from 0.02 to 5 % by weight, based on the monomers to be polymerized.
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The polymerization is to be carried out in the presence of a protective colloid and/or emulsifier suitable for such purposes. Examples of suitable protective colloids are polyvinyl alcohols, cellulose derivatives or polyvinylpyrrolidones. The emulsifiers
5 may be anionic, cationic or nonionic. Examples of suitable emulsifiers are ethoxylated mono-, di- and trialkylphenols, ethoxylated fatty alcohols or sorbitan esters, alkali metal and ammonium salts of alkyl sulfates or alkyl ether sulfates, of alkylsulfonic acids, of ligninsulfonic acid and of
10 alkylarylsulfonic acids or alkyl diphenyl oxidesulfonates.

The emulsion polymerization is conventionally carried out with the exclusion of oxygen and at from 20 to 200°C, either continuously or batchwise.
15

The amounts of monomers and dispersant are expediently chosen so as to give a copolymer dispersion with a concentration of from 30 to 80 % by weight.

20 Preferably, at least some of the monomers, initiators and, if used, regulators are metered uniformly into the reaction vessel in the course of polymerization. However, it is also possible to charge the monomers and the initiator to the reactor and then
25 carry out polymerization, cooling if necessary.

In accordance with one preferred embodiment, the polymerization is carried out using a seed latex, which is expediently prepared in a conventional manner from the monomers which are to be
30 polymerized, in the first polymerization phase. Subsequently, the remaining portion of the monomer mixture is added, preferably by metered addition (feed technique).

35 After the end of polymerization, the residual monomer content can be reduced by carrying out a conventional after-polymerization with the addition of appropriate initiators. If desired, physical deodorization can also take place in a conventional manner by, for example, passing steam into the batch.

40 The pH of the dispersion is adjusted to 4-7, preferably 5-7 and especially 5.5-7 by addition of customary bases, for example an alkali metal hydroxide, such as NaOH, ammonia or organic amines, preferably those which are also used for subsequent
45 neutralization of the carboxyls, in order to make the copolymer easy to wash out. Examples of suitable amines are mono-, di- or trialkanolamines, such as mono-, di- or triethanolamine, triisopropanolamine or 2-amino-2-methylpropanol,

alkanediolamines, such as 2-amino-2-ethylpropane-1,3-diol, or primary, secondary or tertiary alkylamines, such as N,N-diethylpropylamine.

- 5 The adjustment of the pH to 4-7 may also, if desired, be accomplished by adding a buffer solution. Preferred buffers are based on alkali metal and/or ammonium carbonate or bicarbonate.
- 10 The bases and/or buffers are preferably added to the dispersion in the form of dilute aqueous solutions.

The novel copolymers are particularly useful in cosmetology, as film formers. They exhibit a good hairsetting effect and are
15 notable for causing virtually no sticking together of the hairs.

The copolymer dispersion obtainable by the novel process can either be incorporated directly into an aqueous hairsetting formulation or can be dried, for example by spray drying, so that
20 the copolymer can be used as a powder and incorporated into a hair treatment composition.

Powders obtained by drying novel dispersions should preferably be soluble in ethanol so as to be suitable for use in cosmetic
25 formulations for hair.

For use in hair treatment compositions, all or some of the carboxyls in the polymer are neutralized with an alkali metal hydroxide or an amine, expediently to a level of from 30 to
30 100 %, preferably from 50 to 100 %. Amines which can be used are those mentioned above.

The examples which follow illustrate the invention without
35 limiting it. The test data indicated below were obtained as follows:

Shear stability:

- 40 A sample of the dispersion was stirred for 15 minutes at a speed of 9000 rpm. As a measure of the shear stability, the particle size distribution, measured by light scattering, was determined. If a dispersion is shear-stable, there is no significant change in the particle size distribution as a result of the shearing
45 imparted by stirring. If the difference is more than 5 %, the dispersion is unstable to shearing.

Solubility in ethanol:

5 A sample of the dispersion is converted by freeze-drying or spray-drying into a powder, which is dissolved in ethanol (5 % w/w) and neutralized to the extent of 100 % using 2-amino-2-methylpropanol.

10 The test for solubility is made visually. The assessment levels are: clear, almost clear, cloudy and highly cloudy. From the applications standpoint, the classifications clear and almost clear denote acceptability.

Solubility in water:

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The test is similar to that for solubility in ethanol.

pH stability on storage:

20 The pH of the dispersion is measured after storage for 6 months at 25°C. The dispersion is said to be stable on storage if the pH has changed by not more than 0.15 pH units.

Proportion of coagulum:

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The proportion of coagulum in the dispersion, based on the initial weight of monomer, is determined by filtration. Formation of coagulum is deemed to have taken place if the proportion of coagulum is ≥ 0.1 %.

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For the Examples and Comparison Examples described below, a dispersion was prepared as follows:

35 1 g of sodium lauryl sulfate, 6.7 g of a commercial nonionic emulsifier, 100 g of water, 1.3 g of ethylhexyl thioglycolate, 60 g of methacrylic acid, 210 g of tert-butyl acrylate and 30 g of ethyl acrylate are used to prepare an emulsion which was metered by the feed technique, over the course of about 2 hours and at about 75 - 85°C, into a polymerization vessel containing 40 500 g of water. At the same time the initiator, 1 g of sodium persulfate dissolved in water, was likewise run in continuously. After the end of addition, post-polymerization is carried out for 1 - 2 h at the temperature stated.

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This process is modified in accordance with Examples 1 to 5 and Comparison Examples 1 to 4 below.

Example 1

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After the end of polymerization, 2 g of ammonia in the form of an aqueous solution were added to the dispersion. The pH of the solution was 5.8.

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Example 2

After the end of polymerization, 2 g of ammonia in the form of an aqueous solution of ammonium hydrogen carbonate were added to the
15 dispersion. The pH of the solution was 5.8.

Example 3

20 After the end of polymerization, 1.8 g of ammonia were added to the dispersion in the form of an aqueous ammonium carbonate solution. The pH of the solution was 5.7.

Example 4

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After the end of polymerization, 8.5 g of 2-amino-2-methylpropanol were added to the dispersion in the form of an aqueous solution. The pH of the solution was 5.9.

30 Example 5

At the beginning of the polymerization, about 10 % of the monomer emulsion employed was included in the initial charge, and a seed
35 latex was prepared from this using the appropriate portion of initiator solution, in the first polymerization phase. In the second polymerization phase, the remaining monomer mixture and the remaining initiator solution were metered continuously but separately into the initial charge. After the end of
40 polymerization, the pH was adjusted to >5 by adding 2.0 g of ammonia in the form of an aqueous solution.

Comparison Example 1

45 A dispersion was prepared as described in DE-A-43 14 305, Example 2, without any modification to the pH.

Comparison Example 2

2 g of ammonia in the form of an aqueous solution were added to the emulsion feed stream.

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Comparison Example 3

2 g of ammonia in the form of an aqueous solution were included in the initial charge.

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Comparison Example 4

1 g each of ammonia in the form of an aqueous solution was added to the emulsion feed stream and to the initial charge.

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Using the dispersions obtained in accordance with the Examples and Comparison Examples, the tests described above were carried out. The results obtained are shown in the table:

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Table

25	Example No.	Shear stability	Solubility in ethanol	Solubility in water	Δ pH	Coagulum
	1	stable	almost clear	clear	< 0.2	< 0.1%
	2	stable	almost clear	clear	< 0.2	< 0.1%
30	3	stable	almost clear	clear	< 0.2	< 0.1%
	4	stable	almost clear	clear	< 0.2	< 0.1%
	5	stable	clear	clear	< 0.2	< 0.1%
35	Comp. Ex.					
	1	unstable	almost clear	clear	0.3	< 0.1%
40	2	stable	highly cloudy	highly cloudy	< 0.2	> 3%
	3	stable	highly cloudy	cloudy	< 0.2	> 3%
	4	stable	highly cloudy	highly cloudy	< 0.2	> 3%

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Comparison Example 1 represents the process described in the prior art (DE-A-43 14 305 and EP-A-646 606). It is evident that this dispersion, although meeting the requirements as regards solubility and the formation of coagulum, is nevertheless
5 inadequate in terms of its shear stability and pH stability.

Comparison Examples 2, 3 and 4 show that, by increasing the pH during the polymerization, it is indeed possible to achieve the desired shear stability and pH stability but only at the expense
10 of a situation where the solubility of the copolymers and the formation of coagulum are no longer in accordance with what is required.

15 In contrast, the dispersions obtained in accordance with the novel process are shear-stable and pH-stable, sufficiently soluble in water and ethanol, and with no coagulum formed. Consequently, requirements which appear mutually contradictory are met simultaneously.

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We claim:

- 5 1. A process for preparing alkali-soluble (meth)acrylate-based copolymers by free-radical emulsion polymerization at a pH <4, which comprises adjusting the pH of the dispersion after polymerization to a level within the range from 4 to 7 by adding a base.
- 10 2. A process as claimed in claim 1, wherein the pH of the dispersion is adjusted to a value in the range from 5 to 7 and in particular from 5.5 to 7.
- 15 3. A process as claimed in claim 1 or 2, wherein the monomers used comprise a mixture of
 - a) from 30 to 72 % by weight of t-butyl acrylate or t-butyl methacrylate or a mixture thereof,
 - 20 b) from 10 to 28 % by weight of acrylic acid or methacrylic acid or a mixture thereof, and
 - c) from 0 to 60 % by weight of at least one further free-radically copolymerizable monomer.
- 25 4. A process as claimed in claim 3, wherein at least one of the monomers (c) produces a homopolymer having a glass transition temperature <30°C.
- 30 5. A process as claimed in claim 3 or 4, wherein the monomers (c) used comprise ethyl acrylate or a mixture of ethyl acrylate and N-t-butylacrylamide.
- 35 6. A process as claimed in any of the preceding claims, wherein the emulsion polymerization is carried out using a seed latex of the monomers to be polymerized.
7. A copolymer obtainable by a process as claimed in any of claims 1 to 6.
- 40 8. The use of a copolymer as claimed in claim 7 in hair treatment compositions, especially as a film former in hairsetting compositions.